Actinium Hydrides $\text{AcH}_{10}$, $\text{AcH}_{12}$, and $\text{AcH}_{16}$ as High-Temperature Conventional Superconductors

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ABSTRACT: The stability of numerous unexpected actinium hydrides was predicted via the evolutionary algorithm USPEX. The electron–phonon interaction was investigated for the hydrogen-richest and most symmetric phases: $\text{R}3\text{m}-\text{AcH}_{10}$, $14/\text{mmm}-\text{AcH}_{12}$, and $\text{P}6\text{m}2-\text{AcH}_{16}$. Predicted structures of actinium hydrides are consistent with all previously studied Ac–H phases and demonstrate phonon-mediated high-temperature superconductivity with $T_\text{c}$ in the range of 204–251 K for $\text{R}3\text{m}-\text{AcH}_{10}$ at 200 GPa and 199–241 K for $\text{P}6\text{m}2-\text{AcH}_{16}$ at 150 GPa, which was estimated by directly solving the Eliashberg equation. Actinium belongs to the series of $d^1$ elements ($\text{Sc}–\text{Y}–\text{La}–\text{Ac}$) that form high-$T_\text{c}$ superconducting (HTSC) hydrides. Combining this observation with previous predictions of $p^0$-HTSC hydrides (MgH$_6$ and CaH$_6$), we propose that $p^0$ and $d^1$ metals with low-lying empty orbitals tend to form phonon-mediated HTSC metal polyhydrides.

Table 1. Most Promising Predicted SC Hydrides from So-Called Lability Belt

<table>
<thead>
<tr>
<th>hydride</th>
<th>electronic configuration of the atom</th>
<th>calculated $T_\text{c}$ K (pressure, GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{ScH}_6$</td>
<td>$[\text{Ar}] 3d^1 4s^2$</td>
<td>130 (200)</td>
</tr>
<tr>
<td>$\text{YH}_{10}$</td>
<td>$[\text{Kr}] 4d^1 5s^2$</td>
<td>326 (300)</td>
</tr>
<tr>
<td>$\text{LaH}_{10}^\alpha$</td>
<td>$[\text{Xe}] 5d^1 6s^2$</td>
<td>286 (250)</td>
</tr>
<tr>
<td>$\text{AcH}_{10}$</td>
<td>$[\text{Rn}] 6d^1 7s^2$</td>
<td>251 (this work)</td>
</tr>
<tr>
<td>$\text{ThH}_{10}$</td>
<td>$[\text{Rn}] 6d^1 7s^2$</td>
<td>221 (100)</td>
</tr>
<tr>
<td>$\text{UH}_{6}$</td>
<td>$[\text{Xe}] 5f^1 6d^1 7s^2$</td>
<td>193 (0)</td>
</tr>
</tbody>
</table>

* “Structure has been confirmed experimentally.$^3$

‡ The computational search for phonon-mediated superconductivity in binary hydrides is coming to a finale. Recent results, presented on the Mendeleev’s table in Figure S1 (see the Supporting Information), show that $p$ elements from groups IIIa–V I a form superconducting (SC) hydrides with an even distributed critical temperature that generally decreases with increasing period number and atomic mass of the hydride-forming atom. A completely different situation takes place for $s$, $d$, and $f$ metals, which form a pronounced belt of high-$T_\text{c}$ superconductivity (groups IIa–IIIb, Figure S1). Recent predictions of potential high-temperature superconductivity in lanthanum and yttrium hydrides (LaH$_6$ and YH$_6$) and hydrides of uranium (UH$_6$, unpublished results), thorium (ThH$_{10}$, unpublished results), and scandium (ScH$_6$) have one thing in common: all of these elements contain almost empty $d$, $f$, or $p$ shells (MgH$_6$, CaH$_6$, and ScH$_6$) and form what we call a “lability belt” (see Table 1), i.e., a zone of elements with electronic structure particularly sensitive to the atomic environment because they have empty low-lying orbitals the population of which depends on crystal field, making strong electron-phonon coupling possible.

Sequential occupation of the electronic orbitals, for example, in the lanthanide series, leads to a systematic decrease of the electron–phonon coupling (EPC) strength.$^4$ A possible explanation is that under high pressure electron shells with different symmetry come closer in energy and $H$ atoms become able to form electron-deficient (e.g., $3c2e^3$) bonds with a central atom using a large number of vacant $p$, $d$, or $f$ orbitals. Increasing the number of electrons on valence orbitals of the central metal atom leads to an increase of the Coulomb electron–electron repulsion that sharply reduces the electron–phonon interaction.

Another factor should also be taken into account. For heavy $s^1$–$s^2$ metals from groups I–IIa (e.g., K, Ca, Sr, Ba), the empty $d$ shells are quite close in energy to the $s$ shell. This means that small structural changes in the environment of the central atom may lead to large relative changes in the energy and occupation of $d$ orbitals. This “lability factor” may help us to understand an unexpected increase of electron–phonon interaction in hydrides of boundary ($s\leftrightarrow p$, $s\leftrightarrow d$, $d\leftrightarrow f$) metals.

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Verification of this hypothesis requires the study of actinide hydrides, as Ac is such a borderline element. Direct analogy of chemical properties, atomic size, electronegativity, and electronic configuration of actinium and lanthanum and recent experimental synthesis of LaH$_{10}$ along with predictions of near-room-temperature superconductivity in LaH$_{10}$ at ultrahigh pressures inspired us to study the phase diagram and possible superconductivity in the Ac–H system.

Actinium (from the Greek ακτίς – shining) is highly radioactive; its longest-lived isotope $^{227}$Ac has a half-life of 22 years and in the bulk phase has a fcc crystal structure. Actinium is chemically active and its properties (valence is 3, atomic radius is 1.88 Å) are similar to lanthanum. Isotope $^{227}$Ac is usually obtained by irradiation of radium with neutrons (or deuterons) in the reactor with a small yield of $\sim$ deuterons) in the reactor with a small yield of $\sim$2.15%. Radioactive decay of $^{227}$Ac predominantly proceeds as $\beta^-$ decay with the formation of $^{227}$Th and further $^{227}$Ra through $\alpha$-decay.

Thus, due to the radioactivity of daughter nuclides, $^{227}$Ac is active as an $\alpha$-emitter and has found application in Ac–Be neutron sources, thermoelectric generators, and nuclear medicine for experimental treatment of some forms of cancer, e.g., myeloid leukemia. Recently, another exciting property of Ac, formation of polycations AcH$_{17}$ with helium, was predicted. This is closely related to synthesis and study of polyhydrides (e.g., XH$_{16}$) as a particular case of polyatomic complexes and its stabilization by pressure or charge.

The superconductivity of metallic actinium under pressure was studied theoretically by Dakshinamoorthy et al., where the critical transition temperature ($T_c$) to the SC state was predicted to be from 5 to 12 K. It was also theoretically found that actinium hydride AcH$_3$ is metallic and undergoes multiple Mn3m $\rightarrow$ P4$_2$/mm $\rightarrow$ Imma $\rightarrow$ P6$_3$/mmc phase transitions at 12, 27, and 68 GPa, respectively. Due to the high cost and radioactivity of actinium, its chemistry has been studied very poorly. In this Letter, we intend to partially fill this gap.

We built the composition–pressure phase diagram (see Figure 1), which shows pressure ranges of stability of all phases found at different pressures. As shown in Figure 1, our calculations correctly reproduce the stability of Mn3m-AcH$_{13}$ and predict 12 new stable phases. Due to the fact that conditionally stable (extremely low-energy metastable) phases can be found in experiment, or even can dominate over thermodynamically stable phases (e.g., ref.13), we extended the stability region for R3m-AcH$_{10}$ and I4/mmm-AcH$_{12}$ to higher pressures, shown in Figure 1 by the yellow gradient and dotted lines.

Detailed information on crystal structures of the predicted phases is summarized in Table S2 (see the Supporting Information). Our calculations show that at zero pressure elemental Ac has a P6$_3$/mmc ($\alpha$-Ac) structure, which is lower in energy than Mn3m-Ac ($\beta$-Ac) by 11 meV/atom and transforms to the Fm3m phase at 3 GPa. At 0 GPa, there are only two stable hydrides, metallic Mn3m-AcH$_3$ and semiconducting Fm3m-AcH$_3$ (DFT band gap is 0.95 eV). Fm3m-AcH$_3$ has a fluorite-type structure with a fcc sublattice of actinium atoms, in which hydrogen atoms occupy all tetrahedral voids. The structure of Fm3m-AcH$_3$ contains an extra H atom in the octahedral void and belongs to the Fe$_3$Al structure type. Phase transitions of actinium dihydride (Fm3m $\rightarrow$ P4$_2$/mm $\rightarrow$ Imma $\rightarrow$ P6$_3$/mmc) predicted in ref 12 turned out to be metastable due to decomposition 2AcH$_3$ $\rightarrow$ AcH + AcH$_3$ in the pressure range of 5–65 GPa (see the Supporting Information).

Fm3m-AcH$_3$ loses its stability at 78 GPa, when it transforms to Cmcm-AcH$_{10}$, which remains stable at least up to 350 GPa (see Figure 1). In this phase, Ac atoms are coordinated by 14 hydrogens (see the Supporting Information). Apart from AcH$_2$ and AcH$_6$, at low pressures (>5 GPa), there is another phase Fm3m-AcH with a rocksalt crystal structure, which decomposes at 125 GPa (2AcH $\rightarrow$ Ac + P6$_3$/mmc-AcH$_3$).

At 25 GPa, a new superhydride Cm2c-AcH$_2$ appears and remains stable up to 100 GPa. In this structure, Ac atoms are surrounded by 10 hydrogen atoms ($d_{Ac-H}$ = 2.15–2.18 Å at 100 GPa); 4 of them are terminal atoms in stretched H$_2$ molecules ($d_{h-H}$ = 0.84 Å compared with $d_{h-H}$ = 0.74 Å in the isolated H$_2$ molecule), while the other 6 atoms are single hydrogens. At 50 GPa, C2/m-AcH$_2$ becomes stable (see Figure 1 and Figure S2), where Ac atoms are connected with six H atoms ($d_{Ac-H}$ = 2.22 Å at 70 GPa) and two stretched H$_2$ molecules ($d_{h-H}$ = 0.85 Å at 70 GPa). At 100 GPa, this structure undergoes a phase transition to P6$_3$/mmc-AcH$_{10}$ which loses stability at 180 GPa (see Figures 1 and 2).

At 75 GPa, two new phases, Cmcm-AcH$_{10}$ and Cmcm-AcH$_{12}$ become stable (see Figure 1). Cmcm-AcH$_3$ is stable in a narrow pressure range of 75–100 GPa, whereas Cmcm-AcH$_{10}$, structurally similar to Imma-Th$_3$H$_{10}$ and Imma-U$_3$H$_{10}$
(unpublished results), turns out to be stable at least up to 350 GPa (Figure 1). A structurally similar phase, \( \text{Cm}-\text{AcH}_3 \), differs by a small displacement of hydrogen atoms (Figure 2), which indicates the possibility of easy and reversible transformation of \( \text{AcH}_3 \) to \( \text{AcH}_{10} \) via direct hydrogen saturation under pressure.

New metallic hydride \( \text{C}2/\text{m}-\text{AcH}_3 \) becomes stable at 90 GPa, and its structure contains bent \( \text{H}_2 \) groups (\( d_{\text{H}-\text{H}} = 1.06 \) Å, \( \phi = 122^\circ \) at 150 GPa), and each Ac atom is bonded to three \( \text{H}_2 \) fragments (Supporting Information, Figure S2).

At 80 GPa, actinium decahydride (\( \text{Cm}-\text{AcH}_{10} \)) appears on the phase diagram. At around 140 GPa, it transforms to a more symmetric \( \text{R}3\text{m}-\text{AcH}_{10} \). The stability of \( \text{R}3\text{m}-\text{AcH}_{10} \) is determined by the enthalpy of reaction: \( \text{AcH}_{10} \rightarrow 3\text{AcH}_4 + \text{AcH}_{10} \), which is \( \Delta H = 0.175 \text{ eV at } 150 \text{ GPa} \) (0 K) and \( \Delta H = -1.628 \text{ eV at } 250 \text{ GPa} \) (0 K) when taking into account the zero-point energy (ZPE) contribution. Taking vibrational contribution to the free energy into account, we find that the stability field of \( \text{R}3\text{m}-\text{AcH}_{10} \) expands at room or higher temperatures.

In \( \text{R}3\text{m}-\text{AcH}_{10} \) (150 GPa), the first coordination sphere of Ac contains 14 hydrogen atoms at \( d_{\text{H}-\text{H}} = 2.10 \) Å (see Figure 3a).

The hydrogen environment of Ac atoms in \( \text{I}4/\text{mmm}-\text{AcH}_{12} \) can be described as clathrate-like cage with 40 hydrogen atoms with a diameter of \( \sim 4.47 \) Å (see Figure 4a). The coordination sphere of Ac in \( \text{I}4/\text{mmm}-\text{AcH}_{12} \) is made of eight \( \text{H}_2 \) atoms (see Figure 4b) at \( d_{\text{Ac-H}} = 2.06 \) Å and another eight \( \text{H} \) atoms at \( d_{\text{H-H}} = 2.11 \) Å at 150 GPa. The connection between \( \text{AcH}_{10} \) (Figure 4b) is carried out via \( \text{H}_4 \) tetrahedra with \( d_{\text{H-H}} = 1.45 \) Å, but the minimum \( \text{H-H} \) distance in \( \text{AcH}_{12} \) is in almost linear (\( \phi = 170^\circ \)) \( \text{H}_3 \) fragments with \( d_{\text{H-H}} = 0.94 \) Å (see Figure 4b,c).

An interesting metallic \( \text{P}6\text{m}2\text{-AcH}_{16} \) phase is found to be stable at 110 GPa, in which Ac atoms are coordinated by 12 hydrogens with \( d_{\text{Ac-H}} = 2.08 \) Å at 150 GPa (see Figure 5a). Extension of the radius of the coordination sphere up to 2.16 Å leads to addition of 12 more \( \text{H} \) atoms to the coordination sphere (Figure 5b). These 12 \( \text{H} \) atoms form 6 \( \text{H}_2 \) molecules (\( d_{\text{H-H}} = 0.87 \) Å). Thus, in \( \text{[Ac(hex-H)_2]}(\text{H}_2)_a \) Ac atoms along with 24 bounded \( \text{H} \) atoms form the hexagonal lattice shown in Figure 5d.

Among all predicted hydrogen-rich phases, only two are semiconducting (\( \text{C}2/\text{m}-\text{AcH}_3 \) and \( \text{Cm}-\text{AcH}_3 \)) with DFT band gaps of 0.56 and 1.58 eV, respectively; the systematic underestimation of the band gap by the DFT-PBE method should be kept in mind (see the Supporting Information for details). The rest of the predicted phases are metallic and are potential high-temperature superconductors. Phonon calculations confirmed that the predicted phases have no imaginary phonon frequencies in their predicted ranges of thermodynamic stability (see the Supporting Information). The most interesting compounds \( \text{AcH}_{12^0} \), \( \text{AcH}_{12} \), and \( \text{AcH}_{16} \) were confirmed to be non-magnetic.

The hydrogen environment of Ac atoms can also be described as clathrate-like cage with 32 hydrogen atoms with a diameter of \( \sim 4.5 \) Å (see Figure 5b). The shortest \( \text{H-H} \) distance is 1.07 Å.

The metastable \( \text{I}4/\text{mmm}-\text{AcH}_{12} \) was studied in the pressure range of 150–300 GPa. The existence of this compound is determined by two possible reactions: \( 3\text{AcH}_{12} \rightarrow 2\text{AcH}_{10} + \text{AcH}_6 \) and \( 2\text{AcH}_{12} \rightarrow \text{AcH}_4 + \text{AcH}_{10} \). Calculations indicate that ZPE and thermal contributions play a minor role here, and \( \text{AcH}_{12} \) remains metastable (above the convex hull by 0.05–0.06 eV/atom).

The hydrogen environment of Ac atoms in \( \text{I}4/\text{mmm}-\text{AcH}_{12} \) can be described as clathrate-like cage with 40 hydrogen atoms with a diameter of \( \sim 4.47 \) Å (see Figure 4a). The coordination sphere of Ac in \( \text{I}4/\text{mmm}-\text{AcH}_{12} \) is made of eight \( \text{H}_2 \) atoms (see Figure 4b). At 150 GPa, another eight \( \text{H} \) atoms at \( d_{\text{H-H}} = 2.11 \) Å are bonded to Ac atoms, making the coordination sphere of Ac in \( \text{I}4/\text{mmm}-\text{AcH}_{12} \) stable at 110 GPa, in which Ac atoms are coordinated by 12 hydrogens with \( d_{\text{Ac-H}} = 2.08 \) Å at 150 GPa (see Figure 5a). Extension of the radius of the coordination sphere up to 2.16 Å leads to addition of 12 more \( \text{H} \) atoms to the coordination sphere (Figure 5b). These 12 \( \text{H} \) atoms form 6 \( \text{H}_2 \) molecules (\( d_{\text{H-H}} = 0.87 \) Å). Thus, in \( \text{[Ac(hex-H)_2]}(\text{H}_2)_a \) Ac atoms along with 24 bounded \( \text{H} \) atoms form the hexagonal lattice shown in Figure 5d.

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\( T_c \) was calculated using the “full” Allen–Dynes formula (see eq 1) and the Allen–Dynes modified McMillan formula; see Table 2. We calculated the Eliashberg function \( \alpha^2 F(\omega) \) at different pressures (see the Supporting Information). One can note that an increase of pressure leads to shifting of the \( \alpha^2 F(\omega) \) function to higher frequencies. Our calculations indicate that \( \alpha^2 F(\omega) \) Eliashberg functions of \( \text{R}3\text{m}-\text{AcH}_{10} \) at 200 GPa (see Figure 6a) and \( \text{P}6\text{m}2\text{-AcH}_{16} \) at 150 GPa (see the Supporting Information) have one main “hill”. For this type of \( \alpha^2 F(\omega) \) function, the numerical solution of the Eliashberg equations is well approximated by the full Allen–Dynes formula.\(^{15}\) Calculated \( \lambda \) and \( \omega_{\text{log}} \) as a function of pressure for \( \text{R}3\text{m}-\text{AcH}_{10} \), \( \text{AcH}_{12} \), and \( \text{AcH}_{16} \) are presented in Figure 6b. *The Journal of Physical Chemistry Letters* © 2018 American Chemical Society
AcH_{10}, I_{4}/mmm-AcH_{12}, and P_{6}̅m_{2}-AcH_{16} are summarized in Table 2.

As we mentioned above, the following new stable or conditionally stable phases are metallic and potentially high-\(T_{C}\) superconductors: Cmcm-AcH_{3}, Cmmm-AcH_{10}, Cmcm-AcH_{4}, P1̅-AcH_{5}, C2/m-AcH_{6}, Cm-AcH_{10}, R3m-AcH_{10}, I_{4}/mmm-AcH_{12}, and \(P6̅m_{2}-AcH_{16}\). For AcH_{6}, AcH_{10}, AcH_{12}, and AcH_{16} the EPC coefficient \(\lambda\) exceeds 1.5, and the “full” eq 1 was used for calculating \(T_{C}\).

Cmcm-AcH_{3} is not a superconductor due to the very low EPC coefficient of <0.1 leading to \(T_{C}\) close to 0 K. Calculations of \(T_{C}\) for Cmcm-AcH_{10} and Cmcm-AcH_{12} phases give 3 K (\(\lambda = 0.39\)) and 60 K (\(\lambda = 0.89\)), respectively. This can be explained by the increasing symmetry and hydrogen content versus Cmcm-AcH_{3}. However, an increase in hydrogen content leads to new phenomena in AcH_{5}: there are two stable phases, semiconducting C2/m-AcH_{5} (stable below 100 GPa) and low-symmetry metallic P1̅-AcH_{5} (above 100 GPa), with relatively high SC parameters (\(\lambda = 0.92, \omega_{opt} = 1162\) K). This behavior can be explained by structural differences; in C2/m-AcH_{5}, the hydrogen sublattice consists of H_{2} and isolated H atoms that together forms isolated distorted hexagons, while in P1̅-AcH_{5}.

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Table 2. Predicted SC Properties of Actinium Hydrides

<table>
<thead>
<tr>
<th>phase</th>
<th>(P, \text{GPa})</th>
<th>(\lambda)</th>
<th>(N_{p}) states/atom/eV</th>
<th>(\omega_{opt}) K</th>
<th>(T_{C}) (McMillan), K</th>
<th>(T_{C}) (Allen–Dynes), K</th>
<th>(T_{C}) (Eliashberg), K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cmcm-AcH_{3}</td>
<td>150</td>
<td>0.05</td>
<td>0.094</td>
<td>486</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cmmm-AcH_{10}</td>
<td>150</td>
<td>0.39</td>
<td>0.071</td>
<td>803.6</td>
<td>3 (0.55)</td>
<td>3 (0.55)</td>
<td>3 (0.55)</td>
</tr>
<tr>
<td>Cmcm-AcH_{4}</td>
<td>100</td>
<td>0.89</td>
<td>0.071</td>
<td>982.5</td>
<td>56.5 (41.2)</td>
<td>60 (43.2)</td>
<td>67 (50)</td>
</tr>
<tr>
<td>P1̅-AcH_{5}</td>
<td>150</td>
<td>0.92</td>
<td>0.071</td>
<td>1162</td>
<td>70.5 (49.8)</td>
<td>74.9 (52)</td>
<td>79 (61)</td>
</tr>
<tr>
<td>C2/m-AcH_{6}</td>
<td>150</td>
<td>1.79</td>
<td>0.052</td>
<td>853</td>
<td>113.5 (99.5)</td>
<td>134 (114.1)</td>
<td>149 (134)</td>
</tr>
<tr>
<td>Cm-AcH_{10}</td>
<td>100</td>
<td>2.18</td>
<td>0.057</td>
<td>791.3</td>
<td>120.4 (107.9)</td>
<td>152.1 (130.5)</td>
<td>177 (162)</td>
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<tr>
<td>R3m-AcH_{10}</td>
<td>200</td>
<td>3.46</td>
<td>0.068</td>
<td>710.9</td>
<td>160.9 (125.5)</td>
<td>204.1 (177)</td>
<td>251 (226)</td>
</tr>
<tr>
<td>I_{4}/mmm-AcH_{12}</td>
<td>250</td>
<td>1.96</td>
<td>0.072</td>
<td>812.8</td>
<td>115.3 (102.2)</td>
<td>140.1 (119.7)</td>
<td>176 (151)</td>
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<tr>
<td>P6̅m_{2}-AcH_{16}</td>
<td>300</td>
<td>1.01</td>
<td>0.074</td>
<td>1098</td>
<td>77.3 (59.7)</td>
<td>83.2 (63.3)</td>
<td>101 (76)</td>
</tr>
<tr>
<td>I_{4}/mmm-AcH_{12}</td>
<td>300</td>
<td>1.42</td>
<td>0.041</td>
<td>677</td>
<td>73.4 (62)</td>
<td>83.8 (68.9)</td>
<td>101 (81)</td>
</tr>
<tr>
<td>P6̅m_{2}-AcH_{16}</td>
<td>250</td>
<td>2.16</td>
<td>0.022</td>
<td>1054</td>
<td>159.7 (143)</td>
<td>199.2 (171.3)</td>
<td>241 (221)</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1.34</td>
<td>0.046</td>
<td>1383</td>
<td>140.5 (118.2)</td>
<td>155.9 (128.5)</td>
<td>181 (163)</td>
</tr>
</tbody>
</table>

\(T_{C}\) values are given for \(\mu^*\) equal to 0.1, while \(T_{C}\) values in brackets are for \(\mu^* = 0.15\).

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Figure 6. (a) Eliashberg function \(\alpha^2 F(\omega)\), \(\omega_{opt}\) EPC coefficient \(\lambda\), critical transition temperature \((T_{C})\), and phonon DOS (au) of R3m-AcH_{10} at 200 GPa; (b) \(T_{C}(P)\) functions for R3m-AcH_{10}, I_{4}/mmm-AcH_{12}, and P6̅m_{2}-AcH_{16}.
the hydrogen sublattice consists of bent $H_3$ groups that form infinite hydrogen chains.

The same explanation may be applied for $Cmc_2$, $Ach_1$ (semiconductor, stable at <100 GPa), consisting of isolated $H_2$ and $H_4$ groups, and $C_2/m$-$$Ach_4$ ($\text{metal, stable at >100 GPa}$) with unexpectedly high SC parameters ($\Delta = 1.79$, $T_c = 114–134$ K; see Table 2). $Ach_4$ contains bent $H_4$ groups that form a well-connected branched three-dimensional net.

The highest transition temperature was calculated for $R3m$-$Ach_{10}$ to be in a range from 187 to 204 K at 200 GPa (according to the Allen–Dynes equation), depending on the exact $\mu*$ value (see Table 2 and Figure 6a). Comparison of $\alpha^2F(\omega)$ with the phonon density of states (DOS) (light green) shows that low-frequency modes of the $H_3$ cage provide the main contribution to SC. The effect of high-frequency oscillations of $H_4$ fragments is very weak. Thus, for a certain hydrogen content ($Ach/H = 1:10$), specific for each element, the maximum parameters of the electron–phonon interaction are reached. Further increase of hydrogen content in actinium hydrides ($I4/mmm$-$Ach_{12}$) does not lead to higher $T_c$. Only $P6mm$-$Ach_{16}$ below 150 GPa can achieve 200 K (see Figure 6b). As can be seen from Table 2, in the series of hydrides $Ach_{13}$, the critical temperature increases monotonically as the concentration of hydrogen atoms increases, but further increase of hydrogen concentration leads to decrease of $T_c$ decreasing.

For the hydrogen-richest phases, $R3m$-$Ach_{10}$, $I4/mmm$-$Ach_{12}$, and $P6mm$-$Ach_{16}$, the dependence of EPC parameters on pressure was studied and extrapolated via the well-known empirical equation for low-$T_c$ superconductors,

$$-\ln\left(\frac{T_c}{T_{m0}}\right) = C\nu^\phi, \quad C > 0,$$

where $\nu$ is the volume and $C$ and $\phi$ parameters were calculated earlier for nontransition metals ($\phi = 2.5 \pm 0.6$).\textsuperscript{16,17} The computed decrease of $T_c$ with pressure for $Ach_{10}$, $dT_c/dP = -1.21$ K/GPa (at 250 GPa), is much steeper than for $Ach_{12}$, $dT_c/dP = -0.263$ K/GPa (at 250 GPa), and that for $Ach_{16}$, $dT_c/dP = -0.433$ K/GPa at 250 GPa (see Figure 6b). For comparison, for $CaH_{12}$, $dT_c/dP = -0.33$ K/GPa.\textsuperscript{15} From calculated data (interpolation of the $[T_c/T_{m0}]$ function by the $a \propto b$ law), we can directly determine the coefficients $\phi = 5.53$ ($Ach_{10}$), 0.89 ($Ach_{12}$), and 1.76 ($Ach_{16}$), which are far from the values for low-temperature superconductors. Obtained extrapolation of $T_c(P)$ is shown in Figure 6b. $I4/mmm$-$Ach_{12}$ was found to be the least sensitive to pressure change. The layer-like character of $P6mm$-$Ach_{16}$ leads to substantially higher response to pressure changes in the DOS (increases 2 times in the pressure range of 150–250 GPa) as well as in EPC parameters (see Table 2).

Following the analogy between lanthanum and actinium, in the expected manner, $R3m$-$Ach_{10}$ possesses remarkable high-temperature superconductivity ($T_c = 226–251$ K) and structural similarity to the recently synthesized $LaH_{10}$.\textsuperscript{3} Besides $LaH_{10}$ we found two more SC hydrides: $I4/mmm$-$Ach_{11}$ and $P6mm$-$Ach_{16}$. Similarity of structures of $LaH_{10}$ and $Ach_{10}$ suggests that La may also have hydrides similar to $Ach_{12}$ and $Ach_{16}$ and these ($LaH_{12}$, $LaH_{16}$) compounds as well as $LaH_{10}$ may have been missed by a previous search.\textsuperscript{1}

In conclusion, exploring the analogy between the electronic structure of actinium and lanthanum atoms, we hypothesized that the $Ac–H$ system may have high-$T_c$ SC phases and studied $Ac–H$ system using global optimization within the evolutionary algorithm USPEX at pressures up to 350 GPa.

Five new high-temperature superconductors were predicted, namely $C2/m$-$Ach_{16}$, $Cm$- and $R3m$-$Ach_{10}$, $I4/mmm$-$Ach_{12}$, and $P6mm$-$Ach_{16}$. $Ach_{10}$ is predicted to be SC at temperatures up to 251 K at 200 GPa, $Ach_{16}$ – at temperatures up to 241 K at 110 GPa.

This study is an important part of the work on establishing chemical insight into SC properties of binary metal hydrides, which has a clear correlation with the electronic structure of the hydride-forming metal. Namely, we found that the majority of high-$T_c$ SC hydrides are concentrated near the $d^{10}$ belt of the Periodic Table that is, among metals with minimal number of d and f electrons. With an increasing number of d and f-electrons, SC properties of metal hydrides become less pronounced, possibly due to increasing Coulomb electron–electron repulsion. Large groups of high-temperature hydride superconductors are tied to specific generative metals lying on the junctions ($p–d$, $d–p$) of p, d, and f groups of elements.

This work contributes to the establishment of extreme diversity of actinide hydrides, which, as we have shown earlier (unpublished results), are unexpectedly rich in high-temperature SC phases.

Methods. Evolutionary algorithm USPEX\textsuperscript{19–21} is a powerful tool for prediction of thermodynamically stable compounds of given elements at a given pressure (for some of its application, see refs 22–24). We performed variable-composition searches in the $Ac–H$ system at pressures of 0, 50, 150, 250, and 350 GPa. The first generation (110 structures) was created using a random symmetric generator, while all subsequent generations contained 20% random structures and 80% were created using heredity, softmutation, and transmutation operators.

Here, evolutionary investigations were combined with structure relaxations and total energy calculations using density functional theory (DFT)\textsuperscript{25,26} within the generalized gradient approximation (Perdew–Burke–Ernzerhof functional)\textsuperscript{27} and the projector augmented wave method\textsuperscript{28,29} as implemented in the VASP code.\textsuperscript{30} The plane-wave kinetic energy cutoff was set to 600 eV, and the Brillouin zone was sampled by Γ-centered k-point meshes with resolution $2\pi \times 0.05$ Å\textsuperscript{−1}.

In order to establish stability fields of the predicted phases, we recalculated their enthalpies with increased precision at various pressures with a smaller pressure increment (from 5 to 10 GPa), recalculating the thermodynamic convex hull (Maxwell construction) at each pressure. By definition, the thermodynamically stable phase has lower Gibbs free energy ($G$) and $E_{SC}$ at zero Kelvin, lower enthalpy ($H$) than any phase or phase assembly of the same composition. Phases that were located on the convex hull are the ones stable at a given pressure. Stable structures of elemental $Ac$, $H$, and $Ach_4$ were taken from USPEX calculations and agree with those from refs 13 and 33.

Calculations of SC $T_c$ were carried out using the QUANTUM ESPRESSO package.\textsuperscript{34} Phonon frequencies and EPC coefficients were computed using density functional perturbation theory,\textsuperscript{35} employing the plane-wave pseudopotential method and Perdew–Burke–Ernzerhof exchange–correlation functional.\textsuperscript{27} The effects of core electrons of $Ac$ on valence wave functions were modeled with the aid of scalar relativistic ultrasoft pseudopotentials.\textsuperscript{36} The $6s^2p^6d^7f^2$ electrons of $Ac$ were treated explicitly. Convergence tests showed that 80 Ry is a suitable kinetic energy cutoff for the plane-wave basis set.

Electronic band structures of newly found actinium hydrides were calculated using both VASP and QE and demonstrated good consistency. Comparison of phonon densities of states calculated using a finite displacement method (VASP and
PHONOPY\cite{37,38} and density functional perturbation theory (DFPT) showed perfect agreement between these methods.

The critical temperature was calculated from the Eliashberg equation,\cite{24} which is based on the Fröhlich Hamiltonian $\tilde{H} = \tilde{H}_f + \sum_{\mathbf{q},\omega} \tilde{g}^{(q)}_{\mathbf{k}+\mathbf{q},\mathbf{q}} \tilde{e}^+_{\mathbf{q}}(\mathbf{b}^+_{\mathbf{q}}) + \tilde{e}_{\mathbf{q}}$, where $\mathbf{c}^+$ and $\mathbf{b}^+$ relate to creation operators of electrons and phonons, respectively. The matrix element of electron–phonon interaction $\tilde{g}^{(q)}_{\mathbf{k}+\mathbf{q},\mathbf{q}}$ calculated within the harmonic approximation in Quantum ESPRESSO can be defined as $g_{\mathbf{k}+\mathbf{q},\mathbf{k}} = \frac{\hbar}{2M\omega_{\mathbf{q}}} \int \psi^\dagger_{\mathbf{k}}(r) \left\{ \frac{\partial \mu_{\mathbf{q}}}{\partial \omega} \right\} \psi_{\mathbf{k}+\mathbf{q}}(r) \, d^3r$, where $u_q$ is the displacement of an atom with mass $M$ in the phonon mode $q$. Within the framework of the Gor’kov and Migdal approach,\cite{30,41} the correction to the electron Green’s function $\sum(\mathbf{k},\omega) = G_0^{-1}(\mathbf{k},\omega) - G^{-1}(\mathbf{k},\omega)$ caused by interaction can be calculated by taking into account only the first terms of the expansion of electron–phonon interaction in series of $(\omega_{\mathbf{q}}/E_F)$. As a result, it will lead to integral Eliashberg equations.\cite{30}

These equations can be solved by using an iterative self-consistent method for the real part of the order parameter $\Delta(T, \omega)$ (SC gap) and the mass renormalization function $Z(T, \omega)$\cite{42} (see the Supporting Information).

In our ab initio calculations of the EPC parameter $\lambda$, the first Brillouin zone was sampled using a $4 \times 4 \times 4$ q-point mesh and a denser $24 \times 24 \times 24$ k-point mesh (with Gaussian smearing and $\sigma = 0.02$ Ry, which approximates the zero-width limits in the calculation of $\lambda$). The SC transition temperature $T_c$ was also estimated by using two equations: “full” Allen–Dynes and “short” modified McMillan equation.\cite{15} The full Allen–Dynes equation for calculating $T_c$ has the following form:\cite{15}

$$T_c = \omega_{\log} f_{1/2} \exp \left( \frac{-1.04(1 + \lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*} \right)$$ (1)

with

$$f_{1/2} = \left[ 1 + \frac{\lambda}{2.46(1 + 3.8\mu^*)} \right]^{3/2} \times \left[ 1 - \frac{\lambda^2(1 - \omega_{\log}/\omega^2)}{\lambda^2 + 3.312(1 + 6.3\mu^*)^2} \right]$$ (2)

while the modified McMillan equation has the form but with $f_{1/2} = 1$.

The EPC constant $\lambda$, logarithmic average frequency $\omega_{\log}$ and mean-square frequency $\omega_2$ were calculated as

$$\lambda = \int_0^{\omega_{\max}} 2\alpha^2 F(\omega) \, d\omega$$ (3)

and

$$\omega_{\log} = \exp \left( \frac{2}{\lambda} \int_0^{\omega_{\max}} \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln(\omega) \right)$$

$$\omega_2 = \frac{1}{\lambda} \int_0^{\omega_{\max}} \frac{2\alpha^2 F(\omega)}{\omega} \omega^2 \, d\omega$$ (4)

where $\mu^*$ is the Coulomb pseudopotential, for which we used widely accepted lower and upper bounds of 0.10 and 0.15.

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The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b00615.

Crystal data of predicted Ac–H phases, detailed information about the thermodynamical stability of studied phases and calculated densities of electronic and phonon states along with Eliashberg functions (PDF).

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Notes
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| REFERENCES |


